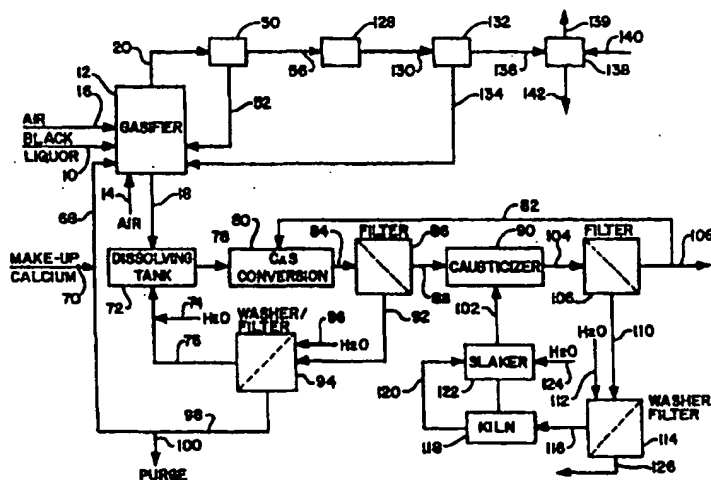




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(54) Title: BLACK LIQUOR GASIFICATION PROCESS AND REGENERATION OF PULPING LIQUOR



(57) Abstract

The black liquor (10) from a kraft pulping process is gasified in a fluidized bed reactor (12) in the presence of solid calcium compounds (CaO , CaCO_3 , Ca(OH)_2) which react with the sulfur compounds (H_2S , COS) to produce solid CaS . The solid CaS along with the other primary solids (Na_2CO_3 , Na_2S) are removed (18) from the reactor (12) and processed to form one or more white liquor streams for recycle to the pulping process. In this processing, the Na_2CO_3 and Na_2S are dissolved (72) to form green liquor and the CaS is reacted (78) with NaOH to form NaHS . The causticizing of the green liquor may be separate from or combined with the conversion of the CaS in the green liquor to form a single white liquor stream (104) or the CaS may be separated from the green liquor and processed entirely separately to form a second high sulfide white liquor stream (174).

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Black Liquor Gasification Process And Regeneration Of Pulping Liquor

Background of the Invention

This invention relates to a system and process for the processing
5 of the spent pulping liquor from a kraft pulping process, known as black
liquor, to recover the chemicals and produce fresh pulping liquor. More
specifically, the system and process involve black liquor gasification in
a fluidized bed reactor to produce a product gas and a dry solids
product, without the formation of any smelt, and then the recovery of
10 the chemicals to produce fresh pulping liquor streams with controlled
compositions.

The kraft pulping process employs an alkaline pulping liquor,
known as white liquor, to react with the lignins in the wood and free
the fibrous portions. Following a series of filtering and washing steps,
15 the fibrous portion is separated as raw pulp and the remaining spent
cooking liquor, which is dark in color, is known as weak black liquor.
This liquor, which is approximately 85% water, is then subjected to a
series of various types of evaporation to produce strong black liquor
with solids content greater than 50%. The strong black liquor is then
20 ready for the chemical recover phase.

The typical prior art process for treating black liquor to recover
chemicals employs what is commonly referred to as a chemical recovery
furnace. In these furnaces, which are operated as boilers for the
generation of steam, the strong black liquor is fired to burn the organic
content and to form a smelt composed primarily of sodium sulfide and
25 sodium carbonate. This smelt is drained from the smelt bed in the
bottom of the furnace, dissolved in water to form green liquor and then
causticized to form the white pulping liquor containing sodium sulfide
and sodium hydroxide.

U.S. Patent 5,284,550 entitled "Black Liquor Gasification Process Operating At Low Pressure Using A Circulating Fluidized Bed," which issued February 8, 1994 and U.S. Patent 5,425,850 entitled "CFB Black Liquor Gasification System Operating At Low Pressures," which issued
5 June 20, 1995 and which are both assigned to the same assignee as the present application, describe and claim one such system and process for replacing a chemical recovery furnace. Referring to the subject matter of U.S. Patents 5,284,550 and 5,425,850, they basically involve the replacement of the chemical recovery furnace with
10 a black liquor gasification system using a circulating fluidized bed reactor arrangement including the arrangement for processing the gases and solids which are produced to generate fresh cooking liquor. In the processes disclosed in these prior patents, kraft black liquor is gasified under substoichiometric conditions to form a product gas rich in sulfide,
15 primarily H_2S with some COS , and a solid bottoms product containing primarily Na_2CO_3 along with some unreacted Na_2SO_4 and some Na_2S . The bottoms product is dissolved to form what is referred to as green liquor which is then reacted to convert the Na_2CO_3 to $NaOH$. This is done by a causticizing process where slaked lime, $Ca(OH)_2$, is added to
20 convert the Na_2CO_3 to $NaOH$ and $CaCO_3$. The solid $CaCO_3$ is then calcined in a kiln to convert it to CaO which is then slaked and recycled to the causticizer. The resulting liquor is referred to as white liquor with a high sodium content and is recycled to the digester. The sulfur-rich product gas is separately processed in a reactor or scrubber to recover
25 the sulfur compounds usually as Na_2S . This sulfur recovery from the product gas may be carried out by wet scrubbing with $NaOH$ and/or Na_2CO_3 or it may be by dry scrubbing with calcium compounds (CaO , $Ca(OH)_2$). In any case, the sulfur in the product gas (H_2S , COS) is converted to high sulfide white liquor containing Na_2S and/or $NaHS$.

Summary of the Invention

The invention involves the gasification of black liquor in a fluidized bed reactor to recover both sodium and sulfur for use in the kraft pulping process. The system will produce solid sodium and solid sulfur compounds in the gasifier suitable for conversion into kraft white liquor. Specifically, the invention employs a calcium reactant which is added to the gasifier to react with the sulfur compounds (H_2S and COS) directly in the gasifier rather than in a separate scrubber/reactor. The calcium reactant may be CaO , CaCO_3 or Ca(OH)_2 including materials which contain these reactants such as limestone and dolomite. The presence of the calcium compounds allows sulfur to be captured in the gasifier at the same time pyrolysis of black liquor occurs. Sulfur reacts with calcium (CaO , CaCO_3 or Ca(OH)_2) to form solid calcium sulfide. The solids from the gasifier containing Na_2CO_3 , Na_2S and CaS , as well as some unreacted calcium compounds, are drained from the gasifier for conversion into kraft pulping liquor. The sodium compounds (Na_2CO_3 and Na_2S) are dissolved to form green liquor containing undissolved calcium compounds. The sodium carbonate is converted to NaOH through standard causticization. Calcium sulfide is converted to sodium hydrosulfide (NaHS) by reaction with sodium hydroxide (NaOH). These processes produce a white liquor suitable for use in kraft pulping.

Brief Description of the Drawings

Figure 1 is a process flow diagram of a black liquor gasification system according to the prior art.

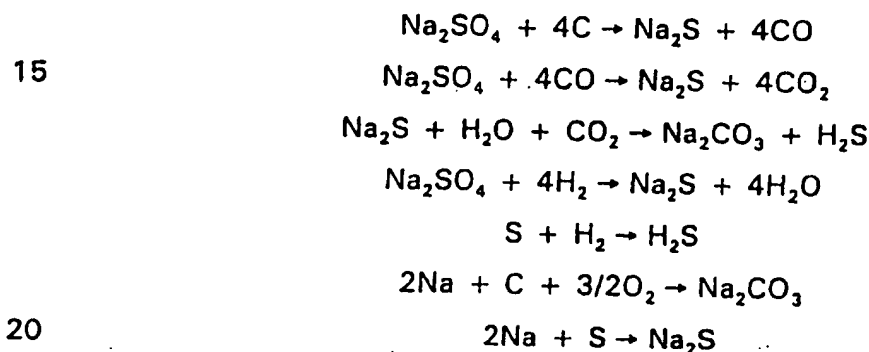
Figure 2 is a process flow diagram illustrating a black liquor gasification system incorporating the present invention.

Figure 3 is a process flow diagram similar to Figure 2 but modified for the combined conversion of CaS and Na_2CO_3 .

Figure 4 is a process flow diagram illustrating a black liquor gasification system according to the present invention modified to provide multiple white liquor streams with variable sulfidity levels.

Description of the Preferred Embodiment

5 Figure 1 is a representation of the process flow diagram for a black liquor gasification system as described in the previously mentioned prior U.S. Patents 5,284,550 and 5,425,850. Strong black liquor 10 derived from the pulp digestion process is fed to the circulating fluidized bed gasifier 12. Fluidizing air 14 and reaction air 16 are also fed into the gasifier 12 as explained by the two prior patents previously identified. The gasification process is carried out with substoichiometric oxygen levels and the primary net reactions with respect to sodium and sulfur which occur in the gasifier are as follows:



The total air to the gasifier is generally in the range of 20% to 50% of stoichiometric which results in the gasification of more than 60% and up to 99% of the sulfur contained in the black liquor. The remaining sulfur reacts with sodium to form Na_2S which remains a solid and is discharged out the bottom along with the Na_2CO_3 and any unreacted Na_2SO_4 . The solids which are formed, primarily Na_2CO_3 , are collected and drained from the bottom of the gasifier as bottoms solids stream 18 while the gas product 20 is removed from the top of the gasifier 12. The gas stream 20 contains sulfur, primarily as H_2S , in

addition to the other products of the substoichiometric oxidation process, namely CO_2 , CO , H_2 , H_2O and N_2 .

The bottoms stream 18 from the gasifier 12, which is a solids stream containing primarily Na_2CO_3 but with some small amount of Na_2S , is fed to the dissolving tank 22. The sodium solids are dissolved in a liquid stream 24 which may be water or a weak liquor or scrubber liquor stream to form green liquor. In any event, the sodium sulfide content of the selected dissolving liquid 24 is low. The resulting green liquor stream 26 contains more than 70% and up to 95% sodium as sodium carbonate on a mole basis.

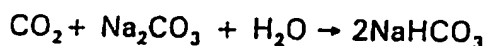
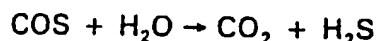
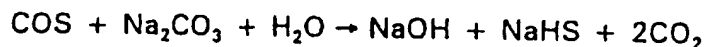
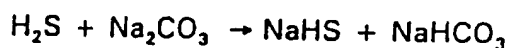
The green liquor stream 26 is fed to the causticizer 28 where slaked lime, $\text{Ca}(\text{OH})_2$, is added from line 30 to convert the Na_2CO_3 to NaOH and CaCO_3 . The slurry 32 from the causticizer 28 is fed to the settling tank 34 where the solids, primarily CaCO_3 , are separated out as a sludge 36 leaving the low sulfide white liquor stream 38. The CaCO_3 sludge 36 is washed with water in the mud washer 40 leaving a weak wash stream 42 which can be used in the plant, as needed. The washed CaCO_3 44 is fed to the kiln 46 for calcining to CaO and then to the slaker 48 for conversion back to $\text{Ca}(\text{OH})_2$. The white liquor stream 38 is composed mainly of NaOH with small amounts of Na_2S and is recycled to the digester.

The gas product 20 from the gasifier 12 would first be cleaned of entrained particulate material at 50 by some form of mechanical separator such as a cyclone with the removed solids being recycled at 52 back to the gasifier. The remaining gas stream from the solids separator means 50 may be cooled at 54 down to the saturation temperature via recovery of heat. If any additional fine dust removal is needed, the gas would then be sent through an electrostatic precipitator, bag filter or some other form of dust removal equipment (not shown). For further details of the mechanical separation, cooling

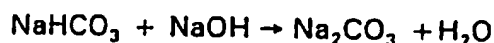
and dust removal, see the previously mentioned prior patents 5,284,550 and 5,425,850.

The cleaned and cooled gas product stream 56 is fed to the sulfur recovery scrubber 58. The scrubber 58, which operates in a known manner, employs a liquor stream 60 containing sodium values (Na_2CO_3 and NaOH) to react with the sulfur compounds, primarily H_2S with some COS , to form a liquor stream 62. Regarding the scrubbing liquor stream 60, it may in fact be several different liquor streams from various sources in the plant. The primary reactions which take place in the scrubber 58 are as follows:

Absorption Reactions



Neutralization Reaction



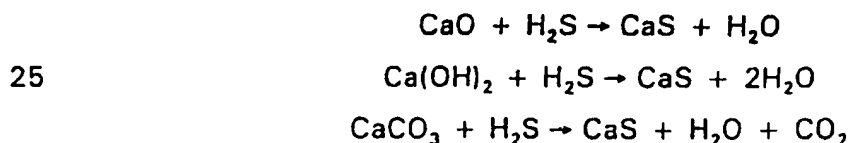
The clean overhead gas 64 from the scrubber 58 now contains primarily CO , CO_2 , H_2 , H_2O , CH_4 and N_2 . There is sufficient heating value in this gas stream 64 so it is typically burned in combustion equipment such as a steam generator or lime kiln. The liquor stream 62 from the scrubber 58 contains primarily Na_2S with smaller amounts of Na_2CO_3 . This green liquor stream 62 is fed to a holding tank 66 from which it is used to prepare a high sulfide white liquor stream which will typically involve another causticizing operation for the Na_2CO_3 .

The present invention improves upon the prior art system of Figure 1 which has just been described in that it provides for the capture of the sulfur in the gasifier and eliminates the requirement for a scrubber/reactor to remove the sulfur from the gases. In the present invention, the gasifier is operated with a bed of particles consisting of

those described in the prior art plus one or more calcium compounds, CaO, Ca(OH)₂ and/or CaCO₃, which react with the sulfur compounds to form CaS.

Referring to Figure 2, the present invention has the same basic arrangement of a circulating fluidized bed gasifier 12 fed with black liquor 10 and fluidizing and combustion air 14 and 16. A similar overhead gas stream 20 is produced and the solids are separated at 50 and recycled back to the gasifier in line 52. This line 52 would actually comprise a conventional solids return system consisting of a discharge duct from the bottom of the separator 50 and a fluidization seal system, known as a G valve or a seal pot. This is to assure one way flow of solids from the separator 50 back to the gasifier. The remaining gas stream 56 will be discussed hereinafter.

The operation of the gasifier in the present invention, as shown in Figure 2, differs from the prior art gasifiers, such as shown in Figure 1, in that calcium compounds are introduced into the gasifier through line 68. The calcium compounds in line 68 comprise recycled calcium compounds and make-up calcium compounds added as needed at 70. The source of the recycle calcium compounds will be apparent from the further description. In the gasifier, the relevant reactions involving the calcium, sodium and sulfur at the substoichiometric, reducing conditions include the gasifier reactions previously indicated plus the following reactions involving the added calcium compounds:



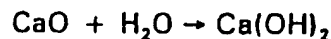
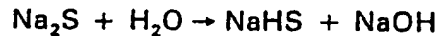
The CO₂ and water vapor which are formed exit with the gas from the top of the gasifier while almost all of the solid compounds which are circulated in the gas stream 20 are separated at 50 and returned to the gasifier 12. Ultimately, the solid compounds exit out of the bottom of the gasifier at 18. The solid product from the gasifier

contains primarily Na_2CO_3 , Na_2S , CaS and any unreacted Na_2SO_4 , CaO and CaCO_3 .

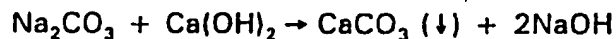
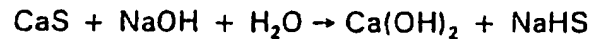
5 The gasifier must be operated in a temperature range where the solids do not melt and agglomerate. Some solid compounds formed in the normal course of black liquor pyrolysis, such as certain sodium and potassium salts, tend to melt at temperatures as low as 500°C to 600°C . The sodium and potassium salts also react with higher melting sodium compounds, Na_2CO_3 (851°C) and Na_2S (1180°C), to form eutectics which lower the bed melting temperature. Such reactions
10 tend to reduce the allowable operating temperature of the gasifier. Generally the gasifier will operate between 650°C and 850°C and most likely between 700°C - 750°C . However, with the circulating solids that includes calcium compounds, the gasifier may be operated at higher temperatures. The presence of the dry, high melting point
15 calcium compounds will counter the agglomerating effect that the melting of other, lower melting solids would have on the fluidization characteristics. First, the dry calcium compounds will bind to and coat any melted compounds so that they will not agglomerate. Second, there will be a dilution of any melted compounds by the dry calcium
20 compounds, so that any agglomeration will be insignificant and will not cause the collapse of the fluidized bed. Third, there may be reactions (unknown) which mitigate the formation of eutectics and raise the bed melting temperature. The advantage of being able to operate the gasifier at a higher temperature is that the reactions involved will
25 proceed at a higher rate. Also, the high temperatures result in high absorption rates of sulfur. Sulfur absorption up to 99% or more may be achieved in the range of 700 to 900°C .

30 The solids stream 18 from the gasifier is fed to the dissolving tank 72. Water, either as make-up water 74 or the weak wash return stream 76, is added to the tank 72 where the Na_2CO_3 and Na_2S are dissolved to form green liquor containing solid CaS , CaO , CaCO_3 and

inert compounds originating from the black liquor. These inert compounds are referred to as ash or non-process elements (NPEs). The CaO hydrates with the water to form Ca(OH)_2 . Sodium sulfide hydrolyzes to form two compounds consisting of sodium hydrosulfide (NaHS) and sodium hydroxide (NaOH). The reactions are as follows:



The liquor stream 78 is fed to a reaction tank 80 to convert the sulfur in CaS into NaHS. White liquor 82 is fed to the tank where the active compound, sodium hydroxide (NaOH), reacts with CaS to form NaHS and calcium hydroxide Ca(OH)_2 . The main reactions occurring during CaS conversion are as follows:



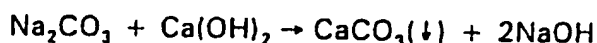
These reactions are time and temperature sensitive. The greatest conversion occurs at temperatures above 80°C. NaOH is required to convert CaS to NaHS and the Ca(OH)_2 is required for the conversion of Na_2CO_3 to NaOH. These reactions complement each other and help minimize the addition of NaOH. Since Na_2CO_3 is far more abundant than CaS, the balance of the Na_2CO_3 is converted in a conventional causticizer.

The effluent green liquor 84 from the CaS conversion at 80 now contains NaOH and NaHS as dissolved compounds plus CaCO_3 , unreacted Ca(OH)_2 and the non-process elements as suspended solids. The green liquor is fed to a solids separation device 86 to clarify the green liquor. Clarified green liquor 88 is discharged and sent to causticizer 90 for final conversion into white liquor.

Solids 92 from filter 86 are washed at 94 with water 96 to remove residual sodium compounds and the solids 98 are returned to the gasifier. The liquid 76 separated from the solids is returned to the dissolving tank 72. The solids 94 returned to the gasifier will contain

non-process elements that flow through the chemical recovery process as inert material. The non-process elements which are contained in the black liquor will build up to high levels if not removed. In order to maintain a low level of non-process elements, the solids stream can be
5 purged at 100 or filtered to maintain the desired level. Make-up calcium 70 will be introduced as required to achieve the required calcium content to the gasifier 12.

The final conversion process to form white liquor occurs in the causticizer 90. Slaked lime ($\text{Ca}(\text{OH})_2$) 102 is fed into the causticizer
10 which converts Na_2CO_3 to NaOH by the following equation:



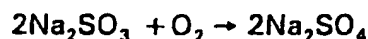
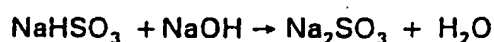
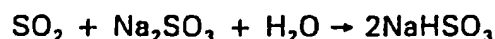
Unclarified white liquor 104 is discharged from the causticizer 90 and sent to a filter 106 to remove the calcium solids. Clarified white liquor 108 is then sent to the digester for pulping of wood. Some white
15 liquor 82 is diverted to the CaS conversion process as previously explained.

Calcium carbonate, which is the primary solid 110 removed from white liquor, is processed through conventional calcining and slaking processes. The CaCO_3 is first washed with water 112 and dewatered
20 in the filter 114. The dewatered CaCO_3 116 is calcined in a lime kiln 118 to produce lime (CaO) 120 which is slaked at 122 with water 124 to form the calcium hydroxide ($\text{Ca}(\text{OH})_2$) 102 for use in the causticizer 90. Liquid 126 taken from the washer 114 may be returned to the dissolving tank 72 or the causticizer 90 as desired.

25 The clean overhead gas 56 from the separator 50 now contains primarily CO , CO_2 , H_2 , CH_4 , H_2O , CH_4 and N_2 and probably some small quantity of unreacted H_2S and COS . There is sufficient heating value in this gas stream 56 so it is burned in the combustion equipment 128
which, for example, could be a steam generator or the lime kiln 118.

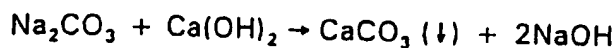
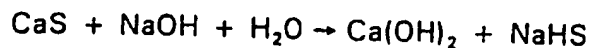
30 The flue gas stream 130 from the combustion equipment 128 is cleaned at 132 to remove any remaining entrained particulate solids which are

recycled at 134 to the gasifier 12 or sent to disposal. The cleaner 132 may be a hot gas filter, a baghouse, an electrostatic precipitation or a wet scrubber. Because there is not 100% H₂S removal in the gasifier 12 and the gas stream 56 contains low concentrations of H₂S which will be oxidized to SO₂ in the combustion equipment 128, the flue gas stream 136 from the cleaner 132 contains some SO₂ which can be vented to the atmosphere if the SO₂ level is low enough or the flue gas can be scrubbed at 138. A scrubbing solution 140, such as a NaOH solution, will convert the SO₂ to Na₂SO₃ and Na₂SO₄. The resulting scrubbing effluent 142 containing the sulfite and sulfate compounds, both of which can be used in pulping, is then returned to the digestion cycle. Production of sodium sulfite can be controlled with the black liquor gasification process by controlling the proportion of sulfur which is gasified as H₂S and other reduced sulfur compounds. This is accomplished by controlling the mole ratio of calcium to sulfur in the reactor. The inclusion of this scrubber 138 reduces the total sulfur emissions from the plant and conserves sulfur for use in the process. The remaining gases 139 from the scrubber 138 may usually be discharged to the atmosphere. The reactions which take place in the SO₂ scrubber 138 are as follows:



If desired, the cleaner 132 may precede the combustion equipment 128.

Figure 3 represents a modified version of the process described in reference to Figure 2 in which both CaS and Na₂CO₃ are converted together. Green liquor 78 containing calcium solids and non-process elements are fed to a conversion process 144 in which the sulfur as CaS is converted to NaHS and the sodium as Na₂CO₃ is converted to NaOH by the following equations:



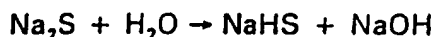
The resulting unclarified white liquor 146 containing calcium solids and non-process elements are filtered at 148 to generate clarified white liquor 150 and solids 152. The solids 152 are washed with water 154 in the washer/filter 156 producing a solids stream 158 primarily of CaCO_3 and a liquid stream 160. The liquid wash stream 160 is returned to the dissolving tank 72 along with whatever additional water may be required.

A standard lime kiln 161 and slaker 162 system regenerates Ca(OH)_2 163 from the CaCO_3 in stream 158 for use in the causticizing of sodium carbonate at 144. The sodium hydroxide generated during this causticizing causes the conversion of CaS to NaHS . Non-process elements contained in washed calcium carbonate stream 158 are purged at 164 before entering the lime kiln 161. Calcium carbonate 68 required to the gasifier is diverted upstream of the kiln 161. Make-up calcium 70 as CaCO_3 , CaO or Ca(OH)_2 is added as required to compensate for calcium lost through purging non-process elements.

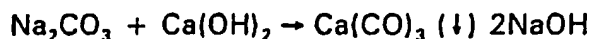
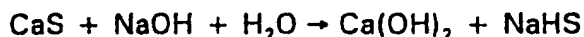
An alternative process for producing the white liquor for use in the digestion process is illustrated in Figure 4. This involves the production of split white liquor streams, one having a low sulfide content and one having a high sulfide content. These split white liquor streams can then be used for a multistage digestion process. A white liquor stream with a high sulfide content is more desirable at the early stages of delignification, while a white liquor with a lower sulfide content and a higher NaOH concentration is more desirable later in the delignification process to more effectively remove lignin without effecting the pulp fiber strength.

In this Figure 4 embodiment, solids 18 containing sodium and calcium compounds plus the non-process elements are discharged from

the gasifier into a dissolving tank 72. The following reactions occur in the dissolving tank 72:



5 Sodium compounds are dissolved to form a green liquor. In order to generate two liquor streams of high and low sulfidity, the calcium solids must be separated from the sodium compounds before CaS is converted by reaction with NaOH. Since NaOH is formed in the dissolving tank when Na₂S is hydrolyzed, some calcium sulfide may
10 begin conversion. If required to slow down the conversion process, the green liquor 78 may be cooled at 165 before entering the solids separation filter 166 where the solid CaS 167 is separated. The solids 167 are discharged into a CaS conversion tank 168 where CaS is converted using NaOH. Most likely, the source of NaOH will be low
15 sulfidity white liquor 170. Water as needed is added at 172. The tank 168 is heated as necessary to a temperature between 80°C and 100°C to promote the following reactions:



20 An unclarified high sulfidity white liquor 174 is discharged from the CaS conversion tank 168 to a filter 176 to separate the calcium solids. Discharged from the filter 176 is a clarified high sulfidity white liquor 178 and solids 180 containing mostly CaCO₃, plus smaller amounts of Ca(OH)₂ and non-process elements. These solids 180, now
25 separated from the high sulfidity white liquor 178 are filtered (washed and dewatered) at 182 with water 184. The liquid 186 which is similar to weak wash is discharged from the filter 182 and recycled back to the dissolving tank 72. Make-up water 74 is added if necessary to this stream 186. The solids 68 discharged from the filter is recycled back
30 to the gasifier with whatever purge 188 may be required as mentioned

earlier. Make-up calcium 70 is again added to the level required in the gasifier.

5 A second white liquor stream containing a low sulfidity (low NaHS) concentration is generated from the green liquor stream 190 discharged from first solids filter 166. This liquor is high in Na_2CO_3 and low in Na_2S . The carbonate must be converted to NaOH. This is done in a conventional causticizing system using the lime kiln 192 and slaker 194 to produce the $\text{Ca}(\text{OH})_2$ stream 196 for the causticizer 198 as more fully described in reference to Figure 2. The liquor 200 from the
10 causticizer 198 is filtered at 202 to give the low sulfidity white liquor stream 204 and the solid CaCO_3 stream 206. A portion 170 of the white liquor 204 is recycled to a CaS conversion tank 168 while the remainder is sent to the pulping process. The solid CaCO_3 stream 206 is washed and filtered at 208 to yield the CaCO_3 stream 210 for the
15 causticizing operation. The wash water 212 from the washer/filler 208 is returned to the dissolving tank 72. As shown, water is supplied to the washer/filter 208 at 214 while water 216 is supplied to the slaker 194.

20 The invention can also produce a third pulping liquor in the form of sodium sulfite (Na_2SO_3). Sulfite is produced from scrubbing SO_2 contained in the flue gas 136 as described previously. The invention not only produces sulfite as a byproduct of gasification, but can also control the quantity of sulfite produced. Sulfur capture in the gasifier is dependent on many factors including temperature, mixing
25 characteristics, gas and particle residence times and ratio of calcium to sulfur (molar basis). For the most part, all of the above factors will be somewhat constant. However, the ratio of calcium to sulfur, also known as the Ca to S mole ratio, can be easily controlled by controlling the feed rate of calcium into the reactor. Reducing the Ca/S mole ratio
30 will reduce sulfur capture as CaS and increase H_2S production.

Increased H_2S production and hence increased SO_2 production allows increased production of sulfite in the SO_2 scrubber 138.

Since the recycled calcium compounds in line 68 are moist, some of the heat in the gasifier is used merely to dry the calcium compounds.

5 Therefore, instead of injecting them directly back into the gasifier, they may be injected through line 69 into the hot product gas from the gasifier. For example, they may be injected into the separator 50 as illustrated in Figure 4 such that the hot gases dry the calcium compounds and then separates them from the gases along with other

10 solids for recycle to the gasifier. Alternatively, they could be injected into a dedicated contact device located in line 56 and then separated from the gases for recycle apart from the recycle 52 of the other solids.

Claims:

1. A process for the recovery of chemicals from the black liquor generated in a pulp delignification process, said recovery process utilizing a circulating fluidized bed reactor and comprising the steps of:
- 5 a. injecting into said fluidized bed reactor and reacting therein said black liquor and substoichiometric reaction air whereby solid Na_2CO_3 , solid Na_2S and a gaseous product containing gaseous H_2S are formed;
- 10 b. injecting a solid calcium compound into said fluidized bed reactor and reacting said calcium compound with said gaseous H_2S to produce solid CaS in said fluidized bed reactor;
- 15 c. discharging solids from said fluidized bed reactor, said solids containing said solid Na_2CO_3 , said solid Na_2S and said solid CaS ;
- d. dissolving said discharged solid Na_2CO_3 and Na_2S in water to form green liquor containing solid CaS ;
- e. reacting said solid CaS with NaOH to form NaHS ; and
- 20 f. processing said green liquor and said NaHS to form at least one white liquor stream.
2. A process as recited in claim 1 wherein said step (e) of reacting and step (f) of processing comprise the steps of recycling a portion of said white liquor containing NaOH to said green liquor containing solid CaS whereby said solid CaS is converted to NaHS in said green liquor and causticizing said green liquor containing said NaHS to form said white liquor stream.
- 25 3. A process as recited in claim 1 wherein said calcium compound is selected from the group consisting of CaO , CaCO_3 , Ca(OH)_2 and mixtures thereof.
- 30

4. A process as recited in claim 1 wherein said step (e) of reacting CaS with NaOH to form NaHS also forms solid Ca(OH)_2 and further including the steps of separating said solid Ca(OH)_2 and recycling said solid Ca(OH)_2 to said fluidized bed reactor.
- 5 5. A process as recited in claim 1 wherein said step (e) of reacting and said step (f) of processing comprise the step of causticizing said green liquor containing solid CaS whereby NaOH is formed and CaS simultaneously reacts with said formed NaOH to form NaHS in said white liquor.
- 10 6. A process as recited in claim 5 wherein said calcium compound is selected from the group consisting of CaO, CaCO_3 , Ca(OH)_2 and mixtures thereof.
7. A process as recited in claim 5 wherein said step (e) of reacting CaS with NaOH to form NaHS also forms Ca(OH)_2 and further including the steps of separating said Ca(OH)_2 and recycling one portion thereof to said fluidized bed reactor and processing another portion thereof for causticizing said green liquor.
- 15 8. A process as recited in claim 1 and further comprising the step of separating said solid CaS from said green liquor prior to step (e) and wherein said step (f) of processing said green liquor comprises the step of causticizing said green liquor with said solid CaS separated out to form a first white liquor and said step (f) of processing said NaHS comprises the step of removing calcium solids and forming a high sulfide second white liquor.
- 20 9. A process as recited in claim 8 and further including the step of cooling said green liquor containing said CaS to minimize conversion of CaS prior to separating said CaS from said green liquor.
- 25 10. A process as recited in claim 4 wherein said gaseous product with said gaseous H_2S removed is discharged from said fluidized bed reactor and wherein said step of recycling said solid
- 30

Ca(OH)_2 to said fluidized bed reactor further includes the step of contacting said solid Ca(OH)_2 with said discharged gaseous product prior to recycling said solid Ca(OH)_2 to said fluidized bed reactor to dry said solid Ca(OH)_2 .

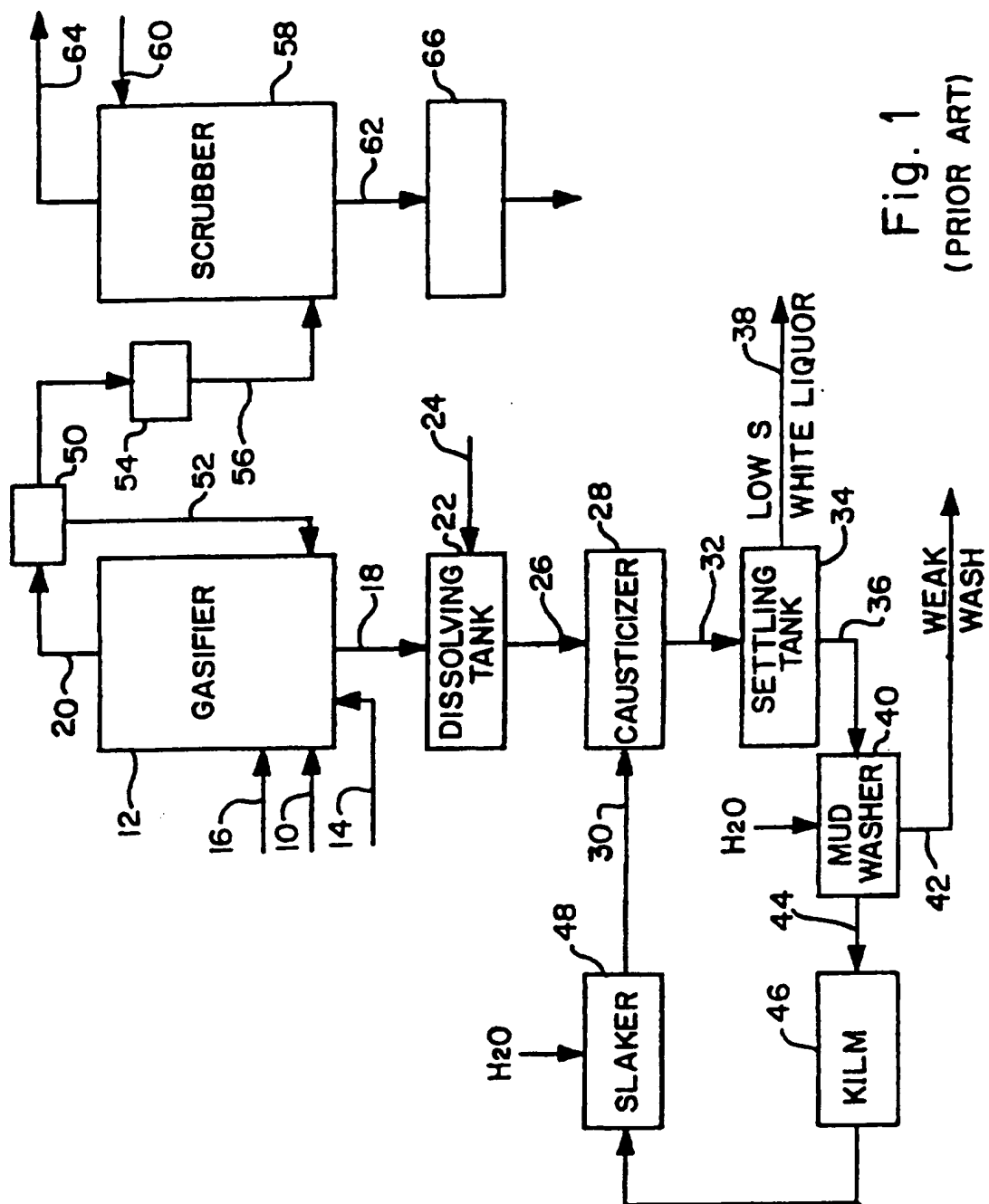


Fig. 1
(PRIOR ART)

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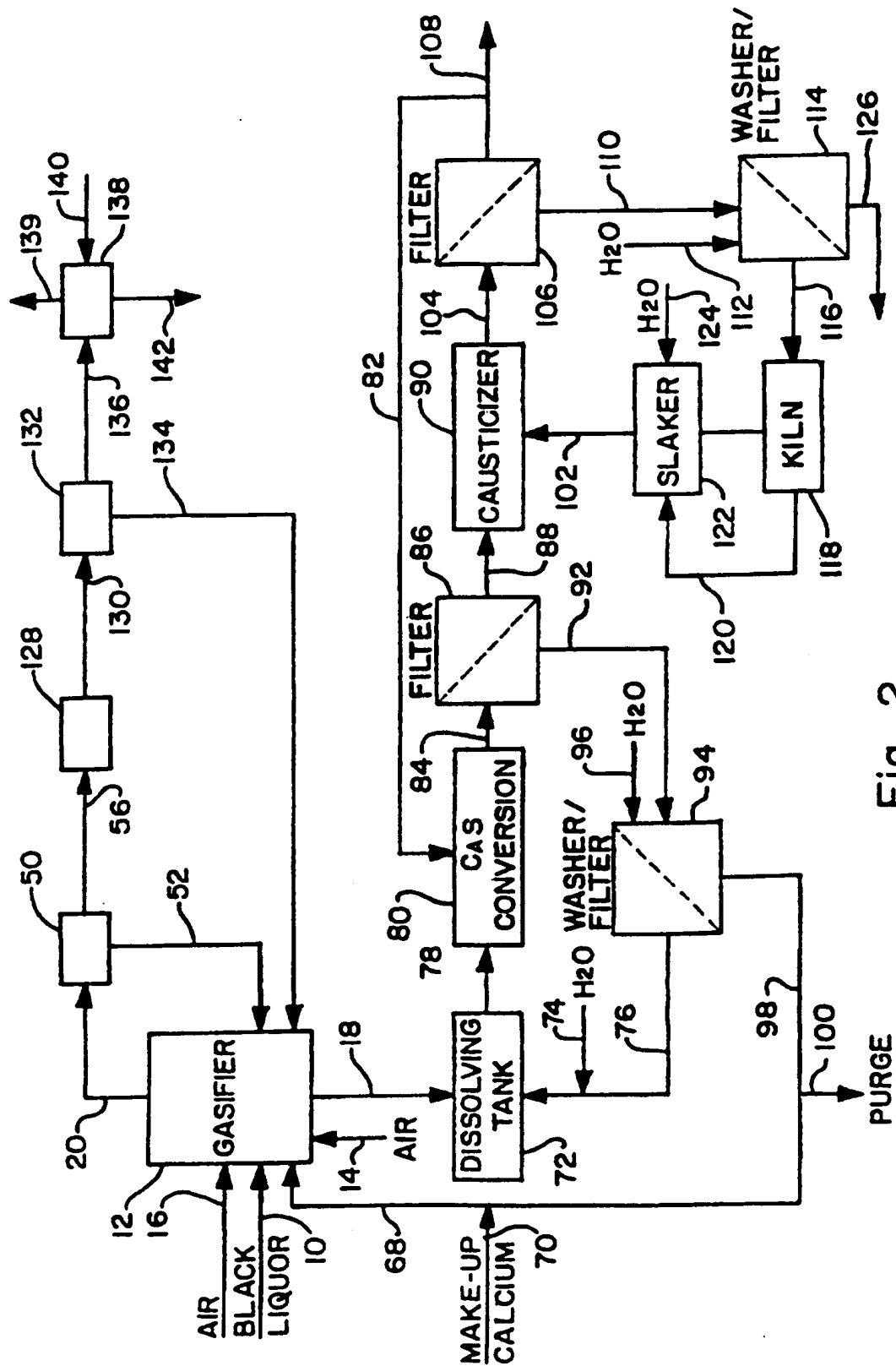


Fig. 2

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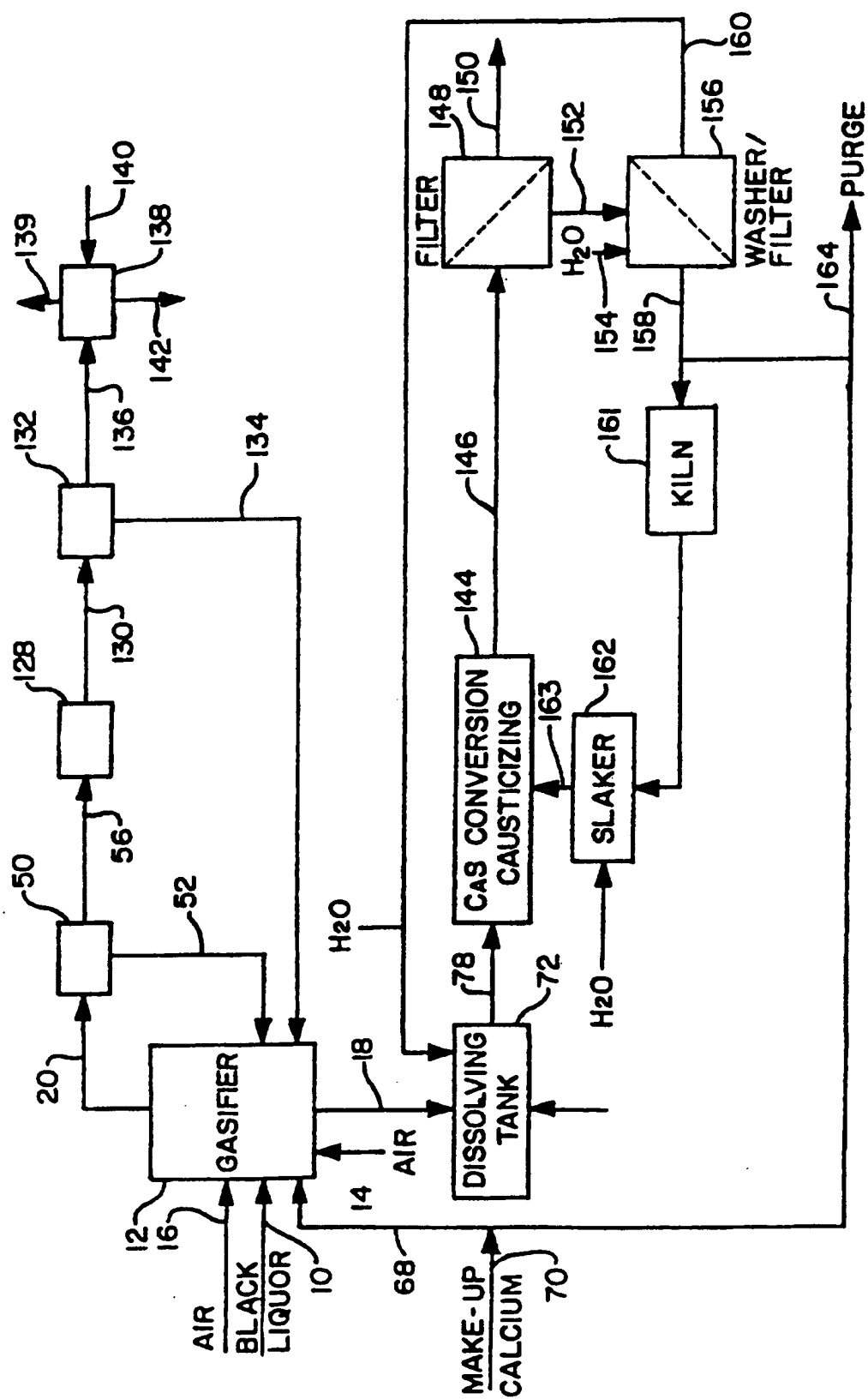


Fig. 3

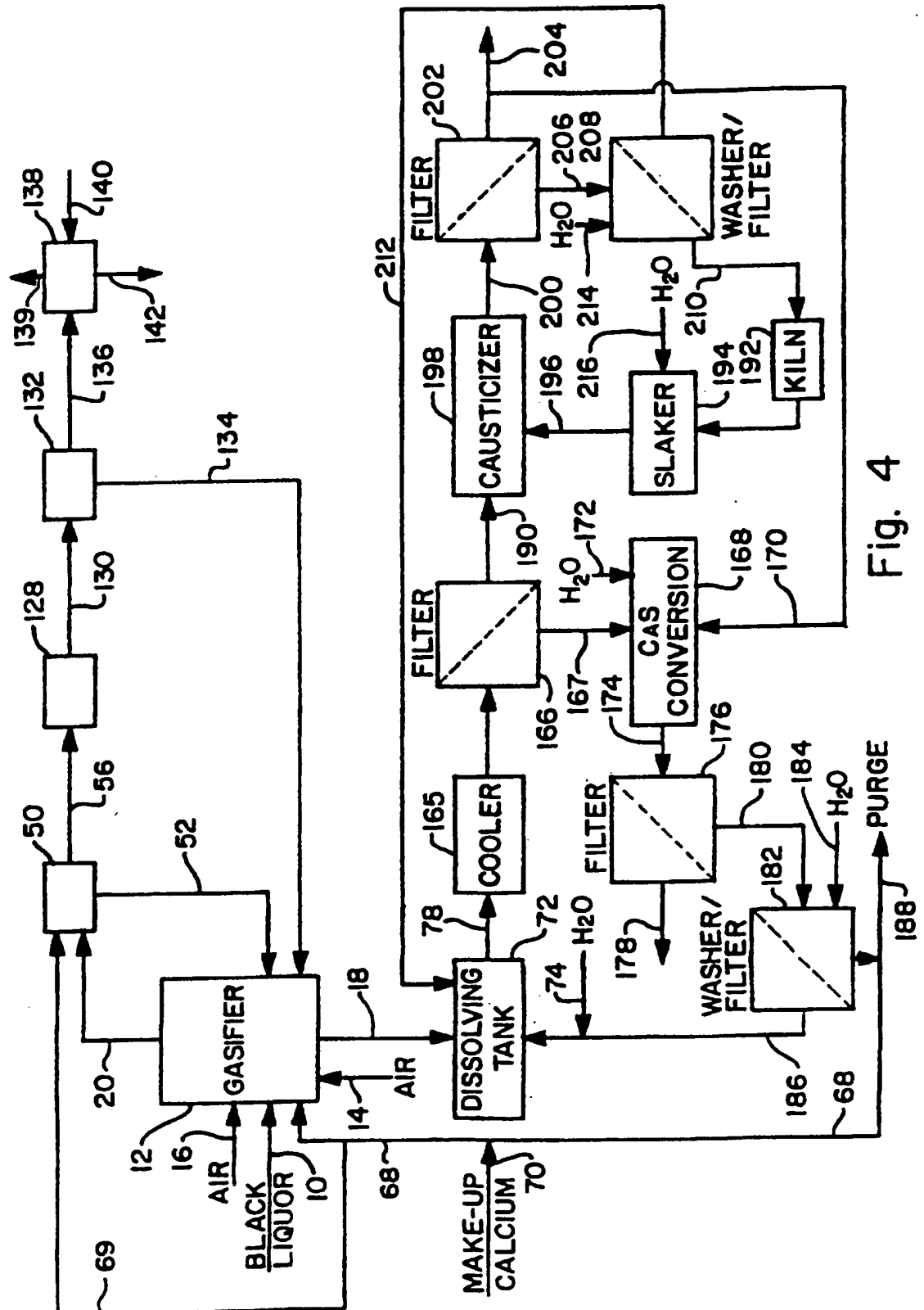


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/U. 96/19091

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C11/12 D21C11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 29516 A (KORSNAES AB) 22 December 1994 see the whole document ---	1-10
Y	US 3 523 864 A (OSTERMAN JOSEPH ET AL) 11 August 1970 see column 5, line 31 - line 38; claims ---	1-10
A	FR 2 550 245 A (NIVELLEAU BRUNIERE PATRICK M F) 8 February 1985 see the whole document ---	1,3-7
A	GB 922 774 A (HANS J. ZIMMER VERFAHRENSTECHNIK) 3 April 1963 see page 2, line 123 - page 3, line 4 -----	1,3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

1 April 1997

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/19091

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9429516 A	22-12-94	SE 501347 C	23-01-95
		CA 2163368 A	22-12-94
		FI 955805 A	01-12-95
		SE 9301921 A	05-12-94
-----	-----	-----	-----
US 3523864 A	11-08-70	NONE	
-----	-----	-----	-----
FR 2550245 A	08-02-85	NONE	
-----	-----	-----	-----
GB 922774 A		NONE	
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